

CORRESPONDENCE/MEMORANDUM**State of Wisconsin**

DATE: September 9, 2019

TO: Nate Willis – WY/3

FROM: Wade Strickland – WY/3

SUBJECT: Water Quality-Based Effluent Limitations for the Superior Refining Company LLC –
Husky Superior Refinery WPDES Permit No. WI-0003085-09-0

This is in response to your request for an evaluation of the need for water quality-based effluent limitations using Chapters NR 102, 104, 105, 106, 207, 210, 212, and 217 of the Wisconsin Administrative Code (where applicable), for the discharge from the Superior Refining Company in Douglas County. This industrial facility discharges to Newton Creek, located in the St. Louis River Watershed in the Lake Superior Basin. The evaluation of the permit recommendations is discussed in more detail in the attached report.

No changes are recommended in the permit limitations for BOD₅, Total Suspended Solids (TSS), pH, or Dissolved Oxygen. Based on our review, the following recommendations are made on a chemical-specific basis:

Outfall 001 – WWTP Effluent

Parameter	Daily Maximum	Daily Minimum	Weekly Average	Monthly Average	Six-Month Average	Footnotes
BOD ₅	30 mg/L			15 mg/L		
TSS	30 mg/L			20 mg/L		
pH	9.0 su	6.0 su				1
Dissolved Oxygen		4.0 mg/L				
Barium			170 ug/L 0.52 lbs/day			2, 3
Ammonia Nitrogen						3
May-September	9.0 mg/L			5.6 mg/L		
October-April	9.0 mg/L					
Phosphorus						4
Interim				1.0 mg/L		
Final				0.225 mg/L	0.075 mg/L 0.15 lbs/day	
Temperature			Limits			5
Chloride						6
Mercury						6
Chronic WET				11 TU _c		7

Footnotes:

1. Effluent pH is allowed to vary outside of this range if the total time of excursions is no greater than 446 minutes per calendar month, no individual excursion is longer than 60 minutes, and no individual excursion goes outside the range of 4.0 – 11.0 s.u. These limits are established according to the technology-based standards in ss. NR 284.12 and NR 205.06 Wis. Adm. Code.
2. A compliance schedule to meet this limit may be appropriate.

3. Additional limits to comply with the expression of limits requirements in ss. NR 106.07 and NR 205.065(7) are not required due to the seasonal nature of the discharge.
4. This current permit includes a compliance schedule to meet the final water quality based effluent limits by April 1, 2021.
5. The following weekly average temperature limits are recommended in the reissued permit. A compliance schedule in the permit to meet these limits may be appropriate.

Month	Weekly Average Effluent Limit (°F)
FEB	54
MAR	57
APR	63
MAY	70
JUN	77
JUL	81
AUG	79
SEP	73
NOV	54

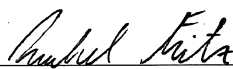
6. Monitoring only.
7. A chronic WET limit of 11 TU_c as a monthly average is recommended in the reissued permit. A minimum of annual chronic WET monitoring is required because of the WET limit. The Instream Waste Concentration to assess chronic test results is 9.1%. The primary control and dilution water used in WET tests conducted on Outfall 001 shall be a grab sample collected from Hog Island Inlet or a standard laboratory water. Tests should be done in rotating quarters, to collect seasonal information about this discharge and shall continue after the permit expiration date (until the permit is reissued).

No acute WET monitoring is recommended in the reissued permit.

Please consult the attached report for details regarding the above recommendations. If there are any questions or comments, please contact Rachel Fritz at (608) 267-7657 (Rachel.Fritz@wisconsin.gov) or Diane Figiel at (608) 264-6274 (Diane.Figiel@wisconsin.gov).

Attachments (3) – Narrative, Thermal Table & Map

PREPARED BY:



Date: 9/9/19

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**Water Quality-Based Effluent Limitations for
The Superior Refining Company LLC**

WPDES Permit No. WI-0003085-09-0

Prepared by: Rachel Fritz

PART 1 – BACKGROUND INFORMATION

Facility Description:

When operating, the Superior Refinery refines up to 50,000 barrels of crude oil per day using vacuum distillation, fluid catalytic cracking, and hydrotreating to produce gasoline, kerosene, diesel fuels, heating oils, fuel oils, liquid petroleum gas, asphalt, flux, and elemental sulfur. The refinery is not currently in operation.

The wastewater treatment plant (WWTP) consists of oil/water separation, flow equalization, dissolved gas floatation, activated sludge, clarification, sand filtration, granular activated carbon (GAC) (as needed), ion exchange resin (as needed), pH neutralization, and mechanical sludge handling. The discharge from Outfall 001 is intermittent based on precipitation and storm water storage inventory.

The Superior Refinery experienced an incident on April 26, 2018 and has not resumed refinery process operations since that date. This has resulted in changes to the types of wastewater currently treated and discharged by the Refinery and modification of the Refinery's plans for future discharges.

- Prior to the incident, the Refinery planned to cease discharge from its wastewater treatment plant to Newton Creek (Outfall 001) prior to this permit reissuance. Now the facility plans to continue discharge through Outfall 001 until wastewater can be routed to the City of Superior. Refinery processes will not resume until Outfall 001 is routed to the city, which is projected to occur in the next two years.
- The facility has requested to also add a discharge of construction storm water to Outfall 001.
- Prior to the incident, the WWTP treated process wastewater, cooling tower blowdown, boiler blowdown, process area stormwater, and water softener reject. Following the incident, process wastewater and cooling tower blowdown are no longer being generated. The WWTP now only treats a reduced flow of boiler blowdown, process area storm water, some ongoing maintenance related liquids, water softener reject, firefighting water, and storm water.
- Granular activated carbon (GAC) and ion exchange resin treatment have been added to the WWTP to be used as needed for PFAS treatment.
- The constructed wetland treatment system is no longer in use due to seasonal waterfowl impacts.
- Outfall 002, which previously discharges stormwater from non-process areas and steam condensate, has been closed. However, the facility has requested to retain this outfall in the current permit.

Due to these changes, only monitoring and flow data reported since June 2018 is considered representative of current conditions at Outfall 001. Outfall 003 (a stormwater retention pond discharge) was not affected by the incident. The discharge from this outfall is solely stormwater runoff with monitoring only for flow rate and oil and grease. Outfall 004 is solely hydrostatic test water; the limits and monitoring requirements for this outfall match those in the Hydrostatic Test Water and Water Supply

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System Water general permit. Limits for Outfalls 003 and 004 are not evaluated in this memo. Attachment #3 is a map of the area showing the approximate location of Outfall 001.

Existing Permit Limitations: The current permit, which expired on March 31, 2019, includes the following effluent limitations.

Outfall 001 – WWTP Effluent

Parameter	Daily Maximum	Daily Minimum	Weekly Average	Monthly Average	Six-Month Average	Rolling 12-Month Average	Footnotes
BOD ₅	30 mg/L			15 mg/L			1
TSS	30 mg/L			20 mg/L			1
pH	11 su	4.0 su					1
Dissolved Oxygen		4.0 mg/L					1
Ammonia Nitrogen							
May-September	9.0 mg/L			5.6 mg/L			
October-April	9.0 mg/L						
Phosphorus							
Interim						1.0 mg/L	2
Final				0.225 mg/L	0.075 mg/L		
Chloride							
Interim	590 mg/L						3
Final			400 mg/L				
Mercury	7.8 ng/L						4
Temperature	86 °F						5

Footnotes:

1. These limitations are not being evaluated as part of this review. Because the water quality criteria (WQC) and receiving water characteristics have not changed, limitations for these water quality characteristics do not need to be re-evaluated at this time.
2. This current permit includes a compliance schedule to meet the final water quality based effluent limits of 0.075 mg/L as a six-month average and 0.225 mg/L as a monthly average by April 1, 2021.
3. The current permit included a compliance schedule for chloride. The 590 mg/L limit was applied until March 1, 2019, when the 400 mg/L limit became effective.
4. This is an alternative effluent limit as part of the mercury variance in the current permit.
5. The current permit included a compliance schedule, and the limit became effective April 1, 2016.

The permit also requires monitoring for Oil & Grease, Sulfur, COD, and several toxic compounds. See the 08 reissuance permit for details.

Receiving Water Information:

- Name: Newton Creek
- Classification: Limited Forage Fish (as listed in ch. NR 104). About 1.5 miles downstream, Newton Creek reaches the Hog Island Inlet and Superior Bay, which is listed as warm water sport fish community, non-public water supply in ch. NR 104. (Cold Water and Public Water Supply criteria

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would be used for bioaccumulating compounds of concern, because the discharge is within the Great Lakes basin.)

- Low Flow: Because this discharge is near the headwaters of Newton Creek, little to no baseflow is available and low flows are assumed to equal zero.
7-Q₁₀ = 0 cfs (cubic feet per second)
7-Q₂ = 0 cfs
- Hardness = Effluent hardness is used in place of receiving water hardness because there is no receiving water flow upstream of the discharge.
- Source of background concentration data: Background concentrations are not included because they don't impact the calculated WQBEL when the receiving water low flows are equal to zero.
- Multiple dischargers: Not applicable
- Impaired water status: Newton Creek is on the 303(d) list of impaired waters. The listed pollutants for the impairment are PAHs, Foam/Floc/Scum/Oil Slicks, and unspecified metals.

Effluent Information:

- Flow Rates (Outfall 001):
Peak 365-day average = 0.235 MGD (Million Gallons per Day)
Peak daily = 0.387 MGD
Peak 7-day average = 0.363 MGD
Peak 30-day average = 0.309 MGD
For reference, the actual average flow from June 2018 to June 2019 was 0.229 MGD.
- Hardness = 167 mg/L as CaCO₃. This value represents the geometric mean of data from a single DMR monitoring result, permit application monitoring, and WET testing data from 2016 and 2017.
- Acute dilution factor used: Not applicable – this facility does not have an approved Zone of Initial Dilution (ZID).
- Water Source: Municipal water supply
- Additives: One biocide (chlorine) and eight water quality conditioners. These are evaluated in Part 7.
- Effluent characterization: This facility is categorized as a primary industrial discharger so the permit application required effluent sample analyses for volatile organics, metals, and conventional pollutants. The permit-required monitoring for chloride, As, Cu, Cr, Pb, Hg, Ni, Zn, Se, Ag, PCBs, PAHs and phenols from June 2018 to June 2019 is used in this evaluation. This data is considered representative of current discharge conditions since the incident. Effluent data for substances for which a single sample was analyzed is shown in the tables in Part 2 below, in the column titled "MEAN EFFL. CONC.".

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Sample Results (ug/L)					Average
Sample Date	10/30/2018	04/15/2019	04/18/2019	04/30/2019	
Arsenic	2.6	1.5			2.1
Cadmium	<0.15	0.36			0.18
Copper	<1.1	<1.1			<1.1
Lead	<0.24	0.38			0.19
Nickel	6.1	2.1			4.1
Zinc	9.2	<4.6			4.6
Selenium	1.6	1.1			1.4
Silver	<0.10	0.13			0.065
Antimony		1.2	0.86		1.0
Acenaphthene	0.0083	<0.0061			0.0042
Thallium		0.42	<0.14		0.21
Barium				35.5	35.5
Manganese				11.7	11.7
Molybdenum				46.3	46.3

“<” means that the pollutant was not detected at the indicated level of detection. The mean concentration was calculated using zero in place of the non-detected results.

	Chloride mg/L
1-day P ₉₉	251
4-day P ₉₉	178
30-day P ₉₉	140
Mean	121
Std	42.1
Sample size	87
Range	66.3 - 258

The following table presents the average concentrations and loadings at Outfall 001 from June 2018 to June 2019 for all parameters with limits in the current permit to meet the requirements of s. NR 201.03(6):

Parameter	Average Measurement
BOD ₅ , Total*	1.0 mg/L
COD*	5.9 mg/L
Dissolved Oxygen	8.8 mg/L
Ammonia Nitrogen*	0.025 mg/L
Oil & Grease*	0.16 mg/L
PAHs	0.019 ug/L
Phosphorus, Total*	0.11 mg/L
Total Suspended Solids*	0.25 mg/L
Temperature Maximum	67 °F

Parameter	Average Measurement
pH	7.9 su
Arsenic	2.1 ug/L
Chloride	121 mg/L
Chromium*	0.025 ug/L
Mercury*	0.22 ng/L
Nickel	4.1 ug/L
Selenium	1.4 ug/L
Zinc	4.6 ug/L

*Results below the level of detection (LOD) were included as zeroes in calculation of the average.

PART 2 – WATER QUALITY-BASED EFFLUENT LIMITATIONS FOR TOXIC SUBSTANCES – EXCEPT AMMONIA NITROGEN

In general, permit limits for toxic substances are recommended whenever any of the following occur:

1. The maximum effluent concentration exceeds the calculated limit (s. NR 106.05(3), Wis. Adm. Code)
2. If 11 or more detected results are available in the effluent, the P₉₉ value exceeds the comparable calculated limit (s. NR 106.05(4), Wis. Adm. Code)
3. If fewer than 11 detected results are available, the mean effluent concentration exceeds 1/5 of the calculated limit (s. NR 106.05(6), Wis. Adm. Code)

Acute Limits based on 1-Q₁₀

Daily maximum effluent limitations for toxic substances are based on the acute toxicity criteria (ATC), listed in ch. NR 105, Wis. Adm. Code. Previously daily maximum limits for toxic substances were calculated as two times the ATC. However, changes to ch. NR 106, Wis. Adm. Code (September 1, 2016) require the Department to calculate acute limitations using the same mass balance equation as used for other limits along with the 1-Q₁₀ receiving water low flow to determine if more restrictive effluent limitations are needed to protect the receiving stream from discharges which may cause or contribute to an exceedance of the acute water quality standards.

$$\text{Limitation} = \frac{(\text{WQC}) (Q_s + (1-f) Q_e) - (Q_s - f Q_e) (C_s)}{Q_e}$$

Where:

WQC = Acute toxicity criterion or secondary acute value according to ch. NR 105

Q_s = average minimum 1-day flow which occurs once in 10 years (1-day Q₁₀)

if the 1-day Q₁₀ flow data is not available = 80% of the average minimum 7-day flow which occurs once in 10 years (7-day Q₁₀).

Q_e = Effluent flow (in units of volume per unit time) as specified in s. NR 106.06(4)(d)

f = Fraction of the effluent flow that is withdrawn from the receiving water, and

C_s = Background concentration of the substance (in units of mass per unit volume) as specified in s. NR 106.06(4)(e).

In this case, since low flows are zero, acute limits are set equal to criteria.

The following tables list the water quality-based effluent limitations for this discharge along with the results of effluent sampling for all the detected substances. All concentrations are expressed in term of micrograms per Liter (µg/L), except for hardness and chloride (mg/L) and mercury (ng/L).

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Daily Maximum Limits based on Acute Toxicity Criteria (ATC)

RECEIVING WATER FLOW = 0 cfs, (1-Q₁₀ (estimated as 80% of 7-Q₁₀)).

SUBSTANCE	REF. HARD. mg/L	ATC = MAX. EFFL. LIMIT*	1/5 OF EFFL. LIMIT	MEAN EFFL. CONC.	1-day P ₉₉	1-day MAX. CONC.
Arsenic		340	68.0	2.1		2.6
Cadmium	167	18.5	3.70	0.18		0.36
Chromium	167	2740	548	0.025		0.17
Copper	167	25.1	5.0	<1.1		-
Lead	167	175	35.0	0.19		0.38
Mercury (ng/L)		830	166	0.22		1.04
Nickel	167	723	145	4.1		6.1
Zinc	167	188	37.6	4.6		9.2
Cyanide, Amendable		45.8	9.16	<6.5		-
Chloride (mg/L)		757			251	258
Manganese**		1680	337	11.7		11.7
Phenols**		4460	892	0.17		0.17

*Per the changes to s. NR 106.07(3), Wis. Adm. Code, effective 09/01/2016 consideration of ambient concentrations and 1-Q₁₀ flow rates yields a more restrictive limit than the 2 x ATC method of limit calculation.

**The limit for this substance is based on a secondary value.

Weekly Average Limits based on Chronic Toxicity Criteria (CTC)

RECEIVING WATER FLOW = 0 cfs (25% of 7-Q₁₀)

SUBSTANCE	REF. HARD. mg/L	CTC	WEEKLY AVE. LIMIT	1/5 OF EFFL. LIMIT	MEAN EFFL. CONC.	4-day P ₉₉
Arsenic		152	152	30.4	2.1	
Cadmium	167	3.68	3.68	0.736	0.18	
Chromium	167	201	201	40.1	0.025	
Copper	167	16.0	16.0	3.20	<1.1	
Lead	167	45.9	45.9	9.17	0.19	
Mercury (ng/L)		440	440	88.0	0.22	
Nickel	167	80.4	80.4	16.1	4.1	
Zinc	167	188	188	37.6	4.6	
Cyanide, Amenable		11.5	11.5	2.29	<6.5	
Selenium		46.5	46.5	9.30	1.4	
Chloride (mg/L)		395	395			178
Barium*		171	171	34.2	35.5	
Manganese*		93.5	93.5	18.7	11.7	
Phenols*		2200	2200	439	0.17	

*The limit for this substance is based on a secondary value.

Monthly Average Limits based on Wildlife Criteria (WC)RECEIVING WATER FLOW = 0 cfs (¼ of the 90-Q₁₀)

SUBSTANCE	WC	MEAN BACK- GRD.	MO'LY AVE. LIMIT	1/5 OF EFFL. LIMIT	MEAN EFFL. CONC.	30-day P ₉₉
Mercury (ng/L)	1.3	-	1.30	0.26	0.22	

Monthly Average Limits based on Human Threshold Criteria (HTC)

RECEIVING WATER FLOW = 0 cfs (¼ of the Harmonic Mean)

SUBSTANCE	HTC	MEAN BACK- GRD.	MO'LY AVE. LIMIT	1/5 OF EFFL. LIMIT	MEAN EFFL. CONC.
Antimony	373	-	373	74.6	1.0
Cadmium	370	-	370	74.0	0.18
Chromium (+3)	3818000	-	3818000	763600	0.025
Lead	140	-	140	28.0	0.19
Mercury (ng/L)	1.5	-	1.5	0.30	0.22
Nickel	43000	-	43000	8600	4.1
Selenium	2600	-	2600	520	1.4
Silver	28000	-	28000	5600	0.065
Thallium*	3.5	-	3.5	0.70	0.21

*The limit for this substance is based on a secondary value.

Monthly Average Limits based on Human Cancer Criteria (HCC)

RECEIVING WATER FLOW = 0 cfs (¼ of the Harmonic Mean)

SUBSTANCE	HCC	MEAN BACK- GRD.	MO'LY AVE. LIMIT	1/5 OF EFFL. LIMIT	MEAN EFFL. CONC.
Arsenic	13.3	-	13.3	2.66	2.1

Because only one substance for which Human Cancer Criteria exists was detected, determination of the cumulative cancer risk is not needed per s. NR 106.06(8), Wis. Adm. Code.

Conclusions and Recommendations: Based on a comparison of the effluent data and calculated effluent limitations, effluent limitations are apparently needed for barium.

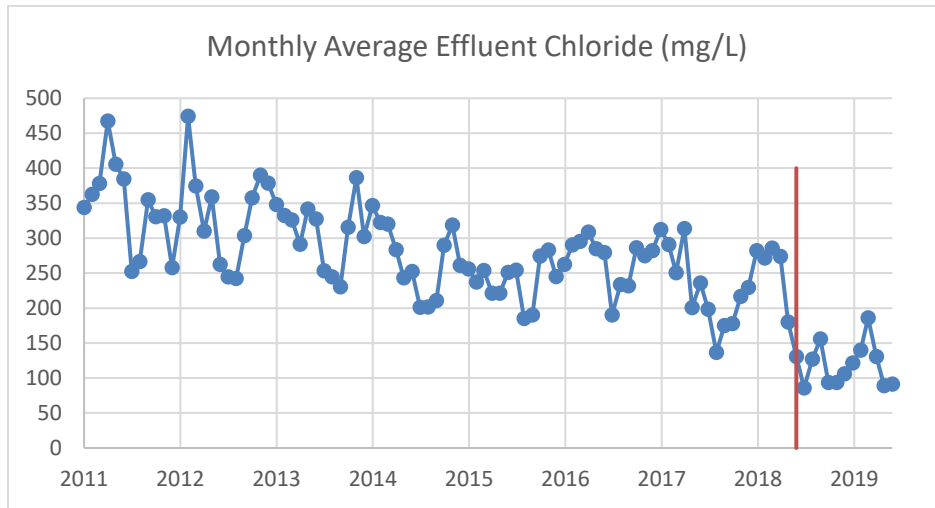
Total Residual Chlorine –Chlorine is added at the facility for cooling tower sanitation. Because cooling tower and boiler blowdown would go through the WWTP and pass through a secondary treatment process no chlorine is expected to be present in the discharge from Outfall 001. Therefore, no chlorine limits are recommended in the reissued permit.

Chloride – The current permit included a compliance schedule for chloride. The final limit of 400 mg/L became effective in March of 2019.

Historically, chloride levels in the discharge have frequently exceeded 400 mg/L during operation. Based on the assessments in Superior Refinery's annual chloride reports, the main source of the chlorides has

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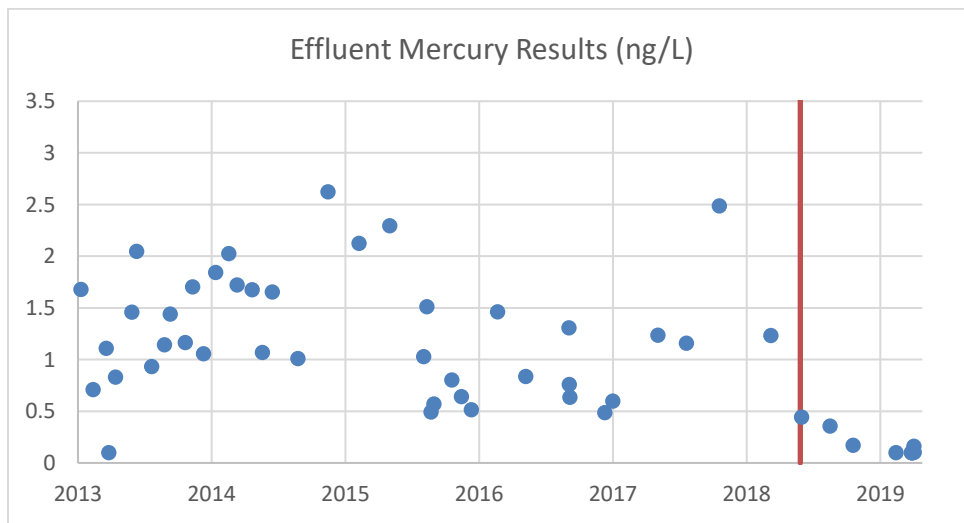
been the desalting process that petroleum goes through to remove impurities including chlorides. Since refining operations ceased since June 2018, chloride levels have dropped significantly as shown below.



Based on effluent chloride data from June 2018 to June 2019, the 1-day P₉₉ value was 251 mg/L and the 4-day P₉₉ value was 178 mg/L. Based on these values, there is not reasonable potential to exceed the calculated chloride limits.

Permit limits typically cannot be dropped if a facility employs a treatment process for removal of the pollutant. The ion exchange resin treatment is used as needed for treatment of PFOS and PFOA, not specifically for chlorides. Discontinuing refining processes has eliminated the major source of chlorides in the discharge. Because the drop in effluent chloride levels is due to a facility process change, **chloride limits may be removed from the reissued permit, however continued monitoring is recommended.**

Mercury – The current permit includes a mercury variance and an alternative effluent limit of 7.8 ng/L. Similarly to chloride levels, effluent mercury levels have dropped significantly since refinery operations ceased in June 2018. The main source of mercury in the discharge was from the petroleum refining operation.



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The average of effluent mercury results since June 2018 is 0.22 ng/L, which is less than one fifth of the calculated limit of 1.3 ng/L, so there is no reasonable potential to exceed the mercury limit. Since there is no treatment for mercury at the facility and the drop in effluent mercury levels is due to a facility process change, **mercury limits may be removed from the reissued permit, however continued monitoring is recommended.**

Barium – A single sample result of 35.5 ug/L was reported with the permit application. This exceeds one fifth of the chronic secondary value of 171 ug/L, which would indicate the need for a limit. Therefore a **weekly average limit of 170 ug/L** (rounded to 2 significant figures) is recommended in the reissued permit. A respective mass limit of **0.52 lbs/day** is also recommended ($0.171 \text{ mg/L} \times 0.363 \text{ MGD} \times 8.34$). A compliance schedule to meet these limits may be appropriate.

Polyaromatic Hydrocarbons (PAH) – Point source wastewater discharges containing PAH compounds are regulated using the best professional judgement (BPJ) technology-based limitation. Compliance can be demonstrated by a no-detect of all PAH compounds or by reporting the sum of the PAH group of 10 detected amounts to be equal to or less than 0.1 µg/L. An alternate method for summing PAH compounds is also available, using a toxicity equivalency factor (TEF) from the document: *PAH Group of 10 Calculation Using Toxicity Equivalent Factors*. The document also includes a BPJ limit of 70 µg/L for Naphthalene.

Since the incident, one PAH test result of 0.02 ug/L and a naphthalene result of 0.011 ug/L are available from 10/20/2018. Since these values are lower than the BPJ limits, no PAH limits are recommended in the reissued permit.

PART 3 – WATER QUALITY-BASED EFFLUENT LIMITATIONS FOR AMMONIA NITROGEN

The State of Wisconsin promulgated revised water quality standards for this substance effective March 1, 2004 which includes criteria based on both acute and chronic toxicity to aquatic life. The current permit includes a daily max limit of 9.0 mg/L and a monthly average limit of 5.6 mg/L in May through September.

The following table evaluates the statistics based upon ammonia data reported from June 2018 to June 2019:

	Ammonia mg/L
1-day P ₉₉	0.31
4-day P ₉₉	0.16
30-day P ₉₉	0.068
Mean*	0.025
Std	0.10
Sample size	87
Range	<0.024 - 0.53

*Values lower than the level of detection were substituted with a zero

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The maximum expected ammonia levels in the discharge are well below any ammonia limits that would be calculated, so ammonia limits are not recalculated in this evaluation.

However, where there are existing ammonia nitrogen limits in the permit, the limits are recommended to be retained regardless of reasonable potential, consistent with s. NR 106.33(1), Wis. Adm. Code:

- (b) If a permittee is subject to an ammonia limitation in an existing permit, the limitation shall be included in any reissued permit. Ammonia limitations shall be included in the permit if the permitted facility will be providing treatment for ammonia discharges.

No changes to the current ammonia limits are recommended.

PART 4 –PHOSPHORUS

Technology Based Effluent Limit (TBL)

Wisconsin Administrative Code, ch. NR 217, requires industrial facilities that discharge greater than 60 pounds of Total Phosphorus per month to comply with a 12-month rolling average limit of 1.0 mg/L, or an approved alternative concentration limit. Because Superior Refinery currently has an existing technology-based limit of 1.0 mg/L, this limit should be included in the reissued permit. This limit remains applicable unless a more stringent water quality-based concentration limit is given.

Water Quality-Based Effluent Limits (WQBEL)

Revisions to administrative rules regulating phosphorus took effect on December 1, 2010. These rule revisions include additions to ch. NR 102 (s. NR 102.06), which establish phosphorus standards for surface waters. Revisions to ch. NR 217 (s. NR 217, Subchapter III) establish procedures for determining water quality based effluent limits for phosphorus, based on the applicable standards in ch. NR 102.

Section NR 102.06(3)(a) specifically names reaches of rivers for which a phosphorus criterion of 0.1 mg/l applies. For other stream segments that are not specified in s. NR 102.06(3)(a), s. NR 102.06(3)(b), Wis. Adm. Code, specifies a phosphorus criterion of 0.075 mg/L. The phosphorus criterion of 0.075 mg/L applies for Newton Creek.

The conservation of mass equation is described in s. NR 217.13 (2)(a), Wis. Adm. Code, for phosphorus WQBELs and includes variables of water quality criterion (WQC), receiving water flow rate (Qs), effluent flow rate (Qe), and upstream phosphorus concentrations (Cs):

$$\text{Limitation} = [(WQC)(Q_s + (1-f) Q_e) - (Q_s - f Q_e) (C_s)] / Q_e$$

Where:

WQC = 0.075 mg/L for Newton Creek.

Qs = 100% of the 7-Q₂

Cs = background concentration of phosphorus in the receiving water pursuant to s. NR 217.13(2)(d), Wis. Adm. Code

Qe = effluent flow rate

f = the fraction of effluent withdrawn from the receiving water = 0

A previous evaluation resulted in a WQBEL of 0.075 mg/L. Since the receiving water flow is equal to zero, the effluent limit is still set equal to criteria. **No changes to the water quality limits of 0.075 mg/L as a six-month average and 0.225 mg/L as a monthly average are recommended in the reissued**

permit. The current permit includes a compliance schedule to meet these limits by 04/01/2021.

Mass Limits

Because the discharge is upstream of a lake, a mass limit is also required, pursuant to s. NR 217.14(1)(a), Wis. Adm. Code. **This final mass limit shall be $0.075 \text{ mg/L} \times 8.34 \times 0.235 \text{ MGD} = 0.15 \text{ lbs/day}$ expressed as a six-month average.**

Effluent Data

The following table summarizes effluent total phosphorus monitoring data from June 2018 to June 2019.

	Phosphorus mg/L
1-day P ₉₉	0.52
4-day P ₉₉	0.29
30-day P ₉₉	0.16
Mean *	0.11
Std	0.11
Sample size	87
Range	<0.038 - 0.57

*Values lower than the level of detection were substituted with a zero

Interim Limit

An interim limit is required per s. NR 217.17 when a compliance schedule is needed in the permit to meet the WQBEL. The interim limit should reflect a concentration that the facility is able to meet without investing in additional “temporary” treatment, but also should prevent backsliding from current conditions. There is relatively little representative phosphorus data available, since only the last year of monitoring may be considered representative of the discharge. Most effluent phosphorus results are very low, but there is also high effluent variability. The maximum monthly average from the last year is 0.32 mg/L, which exceeds the 4-day P₉₉ value (the most frequently used value for phosphorus interim limits). Therefore, **it is recommended that the current interim limit of 1.0 mg/L be continued in the reissued permit.** This interim limit is the same as the currently effective technology-based limit but should be **expressed as a monthly average limit.**

PART 5 –THERMAL

New surface water quality standards for temperature took effect on October 1, 2010. These new regulations are detailed in chs. NR 102 (Subchapter II – Water Quality Standards for Temperature) and NR 106 (Subchapter V – Effluent Limitations for Temperature) of the Wisconsin Administrative Code. Daily maximum and weekly average temperature criteria are available for the 12 different months of the year depending on the receiving water classification.

In accordance with s. NR 106.53(2)(b), the highest daily maximum flow rate for a calendar month is used to determine the acute (daily maximum) effluent limitation. In accordance with s. NR 106.53(2)(c), the highest 7-day rolling average flow rate for a calendar month is used to determine the sub-lethal (weekly average) effluent limitation. These values were based off actual flows reported from June 2018 to June 2019.

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The table below summarizes the maximum temperatures reported during monitoring from June 2018 to June 2019. Comparing the representative highest effluent temperature to the calculated effluent limits determines the reasonable potential of exceeding the effluent limits. The months in which limitations are recommended are highlighted. The complete thermal table used for calculation is attached. Based on this comparison, **weekly average temperature limits are needed in all months except January, October, and December.**

The current permit includes a daily maximum temperature limit of 86 °F, based on limited aquatic life standards for discharge to a wetland. A December 23, 2013 memo stated that the discharge travels through natural wetlands for about 800 ft. Based on photographs from a July 2017 field visit, the receiving water is channelized at the point of discharge. Channelized water bodies are typically categorized as default warmwater sport fishery unless otherwise classified in ch. NR 104. Regardless, if the receiving water is a wetland at the point of discharge, more stringent limits would still be required for protection of the limited forage fish water downstream. Therefore, temperature limits are calculated for protection of limited forage fish uses.

Month	Representative Highest Monthly Effluent Temperature		Calculated Effluent Limit	
	Weekly Maximum	Daily Maximum	Weekly Average Effluent Limitation	Daily Maximum Effluent Limitation
	(°F)	(°F)	(°F)	(°F)
JAN	47	50	54	78
FEB	60	60	54	79
MAR	68	69	57	80
APR	72	77	63	81
MAY	74	76	70	84
JUN	77	81	77	85
JUL	81	85	81	86
AUG	79	82	79	86
SEP	73	77	73	85
OCT	60	66	63	83
NOV	55	63	54	80
DEC	48	49	54	79

Reasonable Potential

Permit limits for temperature are recommended based on the procedures in s. NR 106.56.

- An acute limit for temperature is recommended for each month in which the representative daily maximum effluent temperature for that month exceeds the acute WQBEL. The representative daily maximum effluent temperature is the greater of the following:
 - The highest recorded representative daily maximum effluent temperature
 - The projected 99th percentile of all representative daily maximum effluent temperatures

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- A sub-lethal limitation for temperature is recommended for each month in which the representative weekly average effluent temperature for that month exceeds the weekly average WQBEL. The representative weekly average effluent temperature is the greater of the following:
 - (a) The highest weekly average effluent temperature for the month.
 - (b) The projected 99th percentile of all representative weekly average effluent temperatures for the month

Based on this analysis, **weekly average temperature limits are needed for the months of February-September and November**. A compliance schedule to meet these limits is recommended in the reissued permit. Since Superior Refinery plans to discontinue surface water discharge from Outfall 001, compliance will most likely be resolved by these means.

Otherwise, the following general options are available for a facility to explore potential relief from the temperature limits:

- Effluent monitoring data: Verification or additional effluent monitoring (flow and/or temperature) may be appropriate if there were questions on the representativeness of the current effluent data.
- A variance to the water quality standard: This is typically considered to be the least preferable and most complex option as it requires the evaluation of the other alternatives.
- Monthly low receiving water flows: Contract with USGS to generate monthly low flow estimates for the receiving water to be used in place of the annual low flow.

If low flow estimates are greater than zero:

- Mixing zone studies: A demonstration of rapid and complete mixing may allow for the use of a mixing zone other than the default 25%.
- Collection of site-specific ambient temperature data: This evaluation uses default background temperatures for streams in Wisconsin, so actual data from the direct receiving water may provide for relaxed thermal limits but only if the site-specific temperatures are lower than the small stream defaults used in the above tables

These options are explained in additional detail in the August 15, 2013 document: *Guidance for Implementation of Wisconsin's Thermal Water Quality Standards*

<http://dnr.wi.gov/topic/surfacewater/documents/ThermalGuidance2edition8152013.pdf>

PART 6 – WHOLE EFFLUENT TOXICITY (WET)

WET testing is used to measure, predict, and control the discharge of toxic materials that may be harmful to aquatic life. In WET tests, organisms are exposed to a series of effluent concentrations for a given time and effects are recorded.

- Acute tests predict the concentration that causes lethality of aquatic organisms during a 48 to 96-hour exposure. To assure that a discharge is not acutely toxic to organisms in the receiving water, WET tests must produce a statistically valid LC₅₀ (Lethal Concentration to 50% of the test organisms) greater than 100% effluent.
- Chronic tests predict the concentration that interferes with the growth or reproduction of test organisms during a seven-day exposure. To assure that a discharge is not chronically toxic to organisms in the receiving water, WET tests must produce a statistically valid IC₂₅ (Inhibition Concentration) greater than the instream waste concentration (IWC). The IWC is an estimate of the proportion of effluent to total volume of water (receiving water + effluent). The IWC is 9.1% based on dilution of 10 parts lake

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water to 1-part effluent, or a factor of 1 in 11 to calculate the IWC. The IWC is calculated considering Hog Island Inlet and Superior Bay rather than Newton Creek since this is the first downstream full fish and aquatic life waterbody.

- According to the *State of Wisconsin Aquatic Life Toxicity Testing Methods Manual* (s. NR 219.04, Table A, Wis. Adm. Code), a synthetic (standard) laboratory water may be used as the dilution water and primary control in acute WET tests, unless the use of different dilution water is approved by the Department prior to use. The primary control water must be specified in the WPDES permit.
- According to the *State of Wisconsin Aquatic Life Toxicity Testing Methods Manual* (s. NR 219.04, Table A, Wis. Adm. Code), receiving water must be used as the dilution water and primary control in chronic WET tests, unless the use of different dilution water is approved by the Department prior to use. The dilution water used in WET tests conducted on Outfall 001 shall be a grab sample collected from the receiving water location, upstream and out of the influence of the mixing zone and any other known discharge or a standard laboratory water. The specific receiving water location must be specified in the WPDES permit.
- Shown below is a tabulation of recent WET data for Outfall 001. Efforts are made to ensure that decisions about WET monitoring and limits are made based on representative data. Data which is not believed to be representative of the discharge is not included in reasonable potential calculations. The table below differentiates between tests used and not used when making WET determinations. All WET testing results from prior to the incident (before June 2018) are not considered representative of current discharge conditions.

WET Data History

Date Test Initiated	Acute Results				Chronic Results				Footnotes or Comments
	LC ₅₀ % (% survival in 100% effluent)				IC ₂₅ %				
	<i>C. dubia</i>	Fathead minnow	Pass or Fail?	Used in RP?	<i>C. dubia</i>	Fathead Minnow	Pass or Fail?	Use in RP?	
01/07/2014	>100	>100	Pass	No		>100	Pass		1
02/05/2014					>88		Pass		1
04/15/2014	>100	>100	Pass	No	>88	>88	Pass	No	
08/18/2014	>100	>100	Pass	No	>88	>88	Pass	No	
07/28/2015	>100	>100	Pass	No	>88	>88	Pass	No	
12/06/2016	>100	>100	Pass	No	>88	>88	Pass	No	
05/03/2016					>88	>88	Pass	No	
02/14/2017	>100	>100	Pass	No		>88	Pass	No	2
04/25/2017					67.9		Pass	No	2
04/17/2018	>100	>100	Pass	No	53.1	>88	Pass	No	
05/14/2019	>100	>100	Pass	Yes	25	>88	Pass	Yes	

Footnotes:

1. QA concerns with *C. dubia* test. Redone on 02/05/2014.
 2. 02/14/2017 *C. dubia* test had to be redone. A retest was performed on 03/21/2017 but results were not acceptable due to issues with the *C. dubia* culture. The test criteria on 04/25/2017 were technically met but the accuracy of the results is in doubt and they are not used for reasonable potential determination.
- WET reasonable potential is determined by multiplying the highest toxicity value that has been measured in the effluent by a safety factor to predict the likelihood (95% probability) of toxicity

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occurring in the effluent above the applicable WET limit. The safety factor used in the equation changes based on the number of toxicity detects in the dataset. The fewer detects present, the higher the safety factor, because there is more uncertainty surrounding the predicted value. **WET limits must be given, according to s. NR 106.08(6), Wis. Adm. Code, whenever the applicable Reasonable Potential equation results in a value greater than 1.0.**

According to s. NR 106.08(6)(d), TUa and TUc effluent values are equal to zero whenever toxicity is not detected (i.e. when the LC_{50} , IC_{25} or $IC_{50} \geq 100\%$).

Acute Reasonable Potential = $0 < 1.0$, reasonable potential is not shown and a limit is not required.

Chronic Reasonable Potential = $[(TUc \text{ effluent}) (B)(IWC)]$

TUc (maximum) 100/IC25	B (multiplication factor from s. NR 106.08(6)(c), Wis. Adm. Code, Table 4)	IWC
100/25 = 4.0	6.2 Based on 1 representative detect	9.1%

$$[(TUc \text{ effluent}) (B)(IWC)] = 2.3 > 1.0$$

Therefore, reasonable potential is shown for chronic WET using the procedures in s. NR 106.08(6) and representative data from the last year.

Expression of WET limits

Chronic WET limit = 100/Instream Waste Concentration (IWC) (expressed as a monthly average)
 $= 100/9.1 = 11 TU_c$

The WET Checklist was developed to help DNR staff make recommendations regarding WET limits, monitoring, and other permit conditions. The Checklist steps the user through a series of questions that evaluate the potential for effluent toxicity. The Checklist indicates whether acute and chronic WET limits are needed, based on requirements specified in s. NR 106.08, Wis. Adm. Code, and recommends monitoring frequencies based on points accumulated during the Checklist analysis. As toxicity potential increases, more points accumulate and more monitoring is recommended to ensure that toxicity is not occurring. The completed WET Checklist recommendations for this permittee are summarized in the table below. Staff recommendations, based on the WET Checklist and best professional judgment, are provided below the summary table.

WET Checklist Summary

	Acute	Chronic
AMZ/IWC	Not Applicable. 0 Points	IWC = 9.1%. 0 Points
Historical Data	One representative WET test available 0 Points	One representative WET test (detect) available 0 Points
Effluent Variability	Little variability in the current discharge, no violations or upsets since June 2018 0 Points	Same as Acute. 0 Points
Receiving Water Classification	Less than 4 miles from full fish and aquatic life 5 Points	Same as Acute. 5 Points
Chemical-Specific Data	Limits for zero substances based on ATC; As, Cd, Pb, Hg, Ni, Zn, and chloride detected (3 pts) Additional Compounds of Concern: antimony, selenium, naphthalene and other additional compounds detected (2 pts) 5 Points	Limits for zero substances based on CTC; As, Cd, Pb, Hg, Ni, Zn, Se, and chloride detected (3 pts) Additional Compounds of Concern: antimony, selenium, naphthalene and other additional compounds detected (2 pts) 5 Points
Additives	Several additives used, but only one water quality conditioner is anticipated to possibly be present in the discharge. 1 Point	The water quality conditioner is used more than once per four-day period. 1 Point
Discharge Category	Petroleum refining 15 Points	Same as Acute. 15 Points
Wastewater Treatment	Secondary and additional treatment 0 Points	Same as Acute. 0 Points
Downstream Impacts	No impacts known 0 Points	Same as Acute. 0 Points
Total Checklist Points:	26 Points	26 Points
Recommended Monitoring Frequency (from Checklist):	3 tests during permit term (year 1, 3, 5, etc.)	3 tests during permit term (year 1, 3, 5, etc.)
Limit Required?	No	Yes
TRE Recommended? (from Checklist)	No	No

- According to the requirements specified in s. NR 106.08, Wis. Adm. Code, a chronic WET limit is required. The chronic WET limit should be expressed as **11 TU_c as a monthly average** in the effluent limits table of the permit. **A minimum of annual chronic WET monitoring is required** because of

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the WET limit. Federal regulations in 40 CFR Part 122.44(i) require that monitoring occur at least once per year when a limit is present. Tests should be done in rotating quarters to collect seasonal information about this discharge. WET testing shall continue after the permit expiration date (until the permit is reissued).

- Based upon the point totals generated by the WET Checklist alone, three acute WET tests would be recommended in the reissued permit. However, most of the checklist points come from being placed in the petroleum refining primary industrial category. Since Superior Refinery has ceased refining operations and will not resume until the surface water discharge is discontinued, this industrial category assignment is not entirely appropriate. Considering this, the lack of acute WET failures or detects, and the amount of chronic WET monitoring that is required, **no acute WET monitoring is recommended** in the reissued permit.

PART 7 – ADDITIVE REVIEW

Unlike the metals and toxic substances evaluated in Part 2, most additives have not undergone the level of toxicity testing needed to calculate water quality criteria. Instead, a secondary value can be used to regulate the substance. Whenever an additive is discharged directly into a surface water without receiving treatment or an additive is used in the treatment process and is not expected to be removed before discharge, a review of the additive is needed. Secondary values should be derived according to s. NR 105.05, Wis. Adm. Code.

Additive Name	Manufacturer	Purpose of Additive including where added	Frequency of Use		Estimated Effluent Concentration mg/L	Secondary Acute Value (SAV) mg/L ¹	Secondary Chronic Value (SCV) mg/L ¹
			Months per/yr.	Days/week			
Steamate LSA1791	SUEZ WTS USA, Inc.	Steam condensate treatment	12	7	Not discharged	-	-
Solus AP24	SUEZ WTS USA, Inc.	Internal boiler water treatment	12	7	11.7	459	250
Polyfloc AE1702	SUEZ WTS USA, Inc.	Flocculant	12	7	0.40	0.90	0.205
Phosphoric Acid	Hawkins, Inc.	Microbial nutrient	12	7	Not discharged	Not needed	
Klaraid CDP2727	SUEZ WTS USA, Inc.	Coagulant	12	7	8.3	0.55	0.195
Cortrol OS5700	SUEZ WTS USA, Inc.	Water based DO scavenger	12	7	Not discharged	-	-
Sodium Hydroxide	Hawkins, Inc.	Industrial, mfg., or laboratory use	12	7	Not discharged	Not needed	
Bioplus BA3971	SUEZ WTS USA, Inc.	Bio-augmentation aid	12	7	Not discharged	-	-
Clorox Regular Bleach 5.25%	The Clorox Company	Cooling tower sanitation	5	1	Not discharged	Not needed	

- Calculated based on toxicity data provided. Evaluation are not necessary for additives that have active ingredients consisting only of chlorine, caustic soda (sodium hydroxide), hypochlorite, sulfuric acid, hydrochloric acid

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Secondary values are not calculated for bleach, phosphoric acid, or sodium hydroxide because the discharge of these additives can instead be regulated by permit limits for chlorine, phosphorus and pH.

The estimated effluent concentrations in the table above were provided with the permit application. The facility has an extensive treatment process including oil/water separation, flow equalization, dissolved gas floatation, activated sludge, clarification, sand filtration, granular activated carbon (GAC) (as needed), ion exchange resin (as needed), pH neutralization, and mechanical sludge handling. The coagulant and flocculant (Polyfloc AE1702 and Klaraid CDP2727) are used for solids removal and are intended to be removed with the sludge. Considering that any remaining concentration of these additives would also be treated by sand filtration, and possibly granular activated carbon and ion exchange resin, it's unlikely that any detectable concentration of these products would actually be discharged. A review is not needed because these additives are not expected to be present in the effluent following the treatment process.

Temperature limits for receiving waters with unidirectional flow

(calculation using default ambient temperature data)

Facility:	Superior Refining Company	7-Q₁₀:	0 cfs	Temp Dates		Flow Dates	
Outfall(s):	001	Dilution:	25%	Start:	06/01/18		06/01/18
Date Prepared:	08/15/2019	f:	0	End:	06/20/19		06/20/19
Design Flow (Q_e):	0.235 MGD	Stream type:	Limited forage fish community ▼				
		Qs:Q_e ratio:	0.0 :1				
		Calculation Needed?	YES				

Month	Water Quality Criteria			Receiving Water Flow Rate (Q _s) (cfs)	Representative Highest Effluent Flow Rate (Q _e)		f	Representative Highest Monthly Effluent Temperature		Calculated Effluent Limit	
	T _a (default)	Sub-Lethal WQC	Acute WQC		7-day Rolling Average (Q _{esl})	Daily Maximum Flow Rate (Q _{ea})		Weekly Average	Daily Maximum	Weekly Average Effluent Limitation	Daily Maximum Effluent Limitation
	(°F)	(°F)	(°F)		(MGD)	(MGD)		(°F)	(°F)	(°F)	(°F)
JAN	37	54	78	0	0.205	0.277	0	47	50	54	78
FEB	39	54	79	0	0.246	0.246	0	60	60	54	79
MAR	43	57	80	0	0.277	0.293	0	68	69	57	80
APR	50	63	81	0	0.286	0.305	0	72	77	63	81
MAY	59	70	84	0	0.326	0.364	0	74	76	70	84
JUN	64	77	85	0	0.295	0.317	0	77	81	77	85
JUL	69	81	86	0	0.235	0.249	0	81	85	81	86
AUG	68	79	86	0	0.204	0.222	0	79	82	79	86
SEP	63	73	85	0	0.302	0.332	0	73	77	73	85
OCT	55	63	83	0	0.363	0.387	0	60	66	63	83
NOV	46	54	80	0	0.264	0.296	0	55	63	54	80
DEC	40	54	79	0	0.219	0.290	0	48	49	54	79

Attachment #3

